



The application of Zn–Al-hydrotalcite as a novel anodic material for Ni–Zn secondary cells

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HIGHLIGHTS

- ZnAl-hydrotalcites were proposed as zinc electrode materials for the first time.
- The electrochemical performances of ZnAl-hydrotalcites were firstly investigated.
- ZnAl-hydrotalcites have superior electrochemical cycle stability.
- The sample of Zn/Al = 4/1 (molar ratio) exhibits best electrochemical properties.

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ABSTRACT

ZnAl–CO₃ layered double hydroxides (LDHs) are prepared by the constant pH co-precipitation method in this study and proposed as a novel anodic material for Nickel–Zinc secondary cells. The as-prepared samples are well-crystallized and have the plate-like morphology. It is shown that the reversibility of the electrode reaction of the ZnAl-hydrotalcites is much better than that of ZnO electrode in alkaline system probably due to the lamellar structure of ZnAl-hydrotalcites and the presence of aluminum ions. In spite of a little lower specific capacity, Zn–Al-hydrotalcite electrode has more stable cycling performance, higher charge efficiency and utilization ratio in comparison with ZnO electrode. The effect of Zn/Al molar ratio on the electrochemical performance is investigated and ZnAl-hydrotalcites with Zn/Al molar ratio of 4:1 exhibit the best performance. It delivers an initial discharge capacity of 400 mAh g^{−1} and the capacity retention ratio of 92.7% over 50 cycles. This proves that ZnAl-hydrotalcites electrode is more stable than ZnO electrode in alkaline electrolyte, thus resulting in much better cycling stability.

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1. Introduction

The Ni–Zn alkaline secondary cell is a promising power source for hybrid/electric vehicles and new portable devices. However, the widespread commercial applications of Ni–Zn alkaline secondary cells have been restricted by the poor cycle life of zinc electrode [1–4]. Generally, the shape change of zinc electrode and dendrite growth are the main drawbacks, which are arisen from the high solubility of zinc discharge products and the non-uniform deposition of zinc active material during charging [5–7].

Therefore, it is necessary to find a better and novel anodic material to address such problems. As a class of anionic-exchanging layered material, the layered double hydroxides (LDHs), usually

used as thermal stabilizer, may be an important component of electrode material in respect of the layered structure and large surface area. Its theoretical capacity is more than 440 mAh g^{−1}, larger than that of calcium zincate (342 mAh g^{−1}) [8]. Due to their alkalescence and stability in alkaline solution, they are of importance as anode for alkaline batteries. In Ni–Zn batteries, the ZnAl-hydrotalcites may be a kind of better active material. In the two dimensional layered structures, the zinc hydroxide is arranged orderly on a layer and aluminum hydroxide is on the other parallel layer. The existed aluminum ions may not only reduce the resistivity of zinc active materials but also enhance the electrical conductivity of zinc electrode [9–11]. Consequently, it is significant to restrain zinc dendrite growth and improve electrochemical performance of zinc electrode [11]. Until recently, most of researches have focused on the electrolyte or modification of ZnO, however, there few research on the application of Zn–Al-hydrotalcites as anode material in Zn–Ni secondary cell has been reported. In this paper, the ZnAl-hydrotalcites were proposed as

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zinc electrode materials for the first time and the electrochemical properties were studied in details. For comparison, the electrochemical performance of ZnO electrode was investigated.

2. Experimental

2.1. Preparation of ZnAl-hydrotalcites

The $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR, Tianjin City Guang Fu Fine Chemical Institute) solution was blended with $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR, Tianjin City Fine Chemical Research Institute). Then, the above aqueous mixture and a mixed solution containing NaOH (AR, Tianjin City Fine Chemical Research Institute) and Na_2CO_3 (AR, Tianjin City Fine Chemical Research Institute) were added to the deionized water at a speed of 1 drop/s, respectively. The resultant solution was stirred for 4 h at 85 °C under a constant pH value of 10. Subsequently, the resulting slurry was aged for 20 h at 65 °C. After filtered and washed with distilled water and ethanol, the precipitate was dried and ground to fine powder.

2.2. Characterizations

Fourier transform infrared (FT-IR) spectroscopy were conducted on a Nicolet Nexus-670 FT-IR spectrometer (as KBr discs, with wave number 400–4000 cm^{-1} , resolution 0.09 cm^{-1} , and the weight of measured sample 2 mg). X-ray diffraction (XRD) was performed on a Rigaku D500 (Siemens) diffractometer (36 kV, 30 mA) using Cu K α radiation at a scanning rate of $2\theta = 8^\circ \text{ min}^{-1}$. The morphology of as-synthesized ZnAl– CO_3 –LDHs was observed using scanning electron microscope (SEM, JSM-6360LV).

2.3. Preparation of zinc electrodes and electrochemical measurements

The zinc electrodes were prepared by incorporation slurries containing 80 wt% ZnAl-hydrotalcites, 5 wt% Zn powder (95%, Traditional Chinese Medicines Chemical Reagent), 10 wt% graphite and 5 wt% additives which included 3 wt% polytetrafluoroethylene (PTFE, 60 wt%, in diluted emulsion), 1 wt% In_2O_3 (Tianjin City Fine Chemical Research Institute) and 1 wt% SnO (Hunan Normal University Chemical Reagent Factory, Changsha, China). The addition of In_2O_3 and SnO are for increasing the hydrogen overpotential for zinc electrodes. A copper mesh substrate (2.0 × 2.0 cm in size) served as the current collector. The obtained zinc electrodes were dried at room temperature and then roll-pressed to a thickness of 0.3 mm. The positive electrode was the commercial sintered $\text{Ni}(\text{OH})_2$ (Tianjin City Fine Chemical Research Institute) electrode whose capacity was far higher than those of the zinc electrodes in the aim of making full use of the active material in zinc electrodes. A solution of 5.5 M KOH, 1.0 M NaOH, 0.5 M LiOH was used as the electrolyte.

The cyclic voltammetry test was carried out on electrochemical workstation CS-350 (Wuhan Corrttest Instruments Co.) at room temperature ($25 \pm 1^\circ\text{C}$). A three-electrode cell assembly was used in the test with a Hg/HgO electrode as reference electrode, a commercial sintered $\text{Ni}(\text{OH})_2$ electrode as counter electrode, and a pre-activated zinc electrode as working electrode (2.0 × 2.0 cm in size, a thickness of 0.3 mm). The electrolyte was 6 M KOH solution. Over a shifting range from -1.05 to -1.65 V, cyclic voltammetry (CV) was carried out at a scanning rate of 1 mV s^{-1} .

The galvanostatic charge/discharge cycling tests were performed using BTS-5V/100 mA battery-testing instrument (Neware, China) at room temperature ($25 \pm 2^\circ\text{C}$). The pre-activated zinc electrodes (2.0 × 2.0 cm in size, a thickness of 0.3 mm) were pre-activated for eight times in order to reach ideal discharging

efficiency by the following operations: the cells were charged at 0.1 C for 10 h and discharged at 0.2 C down to 1.4 V cut-off in regular succession. The charge/discharge cycle tests were performed at room temperature.

All of chemical reagents used in this study are of A. R. grade. The deionized water was distilled twice to get rid of carbon dioxide (CO_2).

3. Results and discussion

3.1. FT-IR analysis of ZnAl-hydrotalcites

For the samples of ZnAl-hydrotalcites with different Zn/Al molar ratio, the FT-IR spectra in Fig. 1 were very similar. The broad peak around 3470 cm^{-1} can be ascribed to the stretching of OH^- groups attached to metal ions. The bending vibration of interlayer water is found at 1650 cm^{-1} . The antisymmetric vibration of CO_3^{2-} appears at 1370 cm^{-1} . The lower wave number bands at 400 – 700 cm^{-1} is due to LDH lattice vibrations (M–O). The bands at 775 cm^{-1} and 552 cm^{-1} can be assigned to Al–O stretching modes.

3.2. XRD and SEM analysis of ZnAl-hydrotalcites

Fig. 2(a) shows the XRD patterns of as-prepared ZnAl-hydrotalcites. The characteristic peaks of ZnAl-hydrotalcites are at 11.2° , 23.5° , 35.1° , 61.8° , which correspond to the reflections of (003), (006), (009) and (110) in Fig. 2(a). The highest diffraction peak appears at $2\theta = 11.2^\circ$, suggesting the Zn–Al–LDHs is highly crystallized hydrotalcite-like compound and a typical hexagonal crystal structure. These diffraction peaks are sharp, narrow and symmetrical with a low and stable baseline, indicating that the sample is well-crystallized. Note that the XRD patterns of ZnAl-hydrotalcites with different Zn/Al molar ratios are similar. The results indicate that ZnAl-hydrotalcites could be successfully synthesized with different Zn/Al molar ratios. The typical SEM image of ZnAl-hydrotalcite was presented in Fig. 2(b). It can be seen that the existing lamellar particles have a rounded hexagonal shape, which is the typical structure of the hydrotalcite-like material.

3.3. Cyclic voltammetry (CV) of zinc electrodes

Cyclic voltammetry (CV) experiment was performed in order to comprehend the effect of ZnAl-hydrotalcites on the performance of

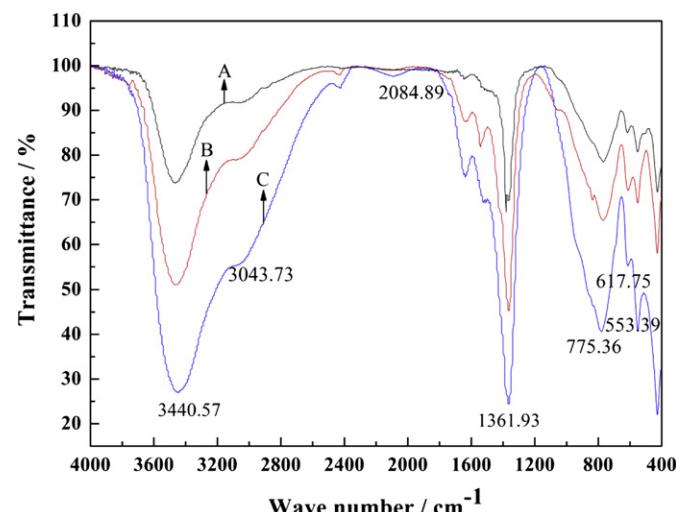


Fig. 1. FT-IR spectra of ZnAl-hydrotalcites with different Zn/Al molar ratio. A: Zn/Al = 3:1. B: Zn/Al = 4:1. C: Zn/Al = 5:1.

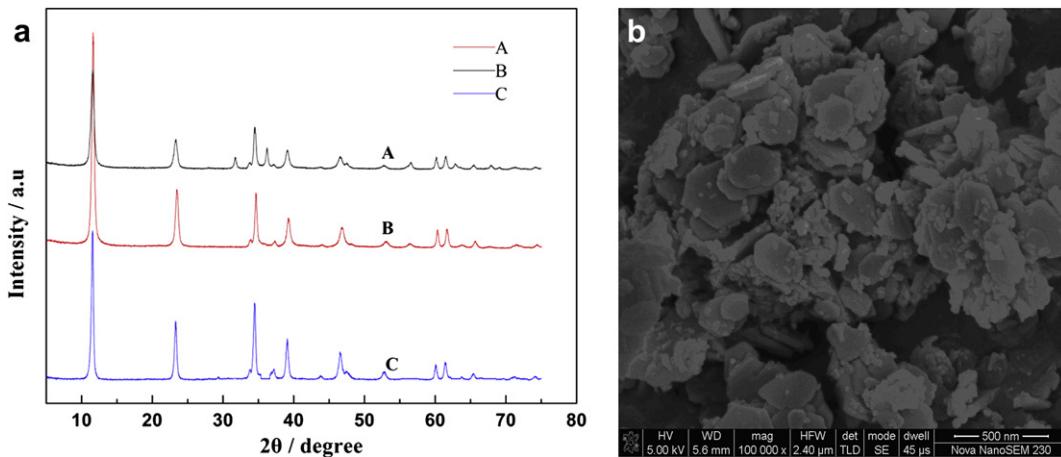
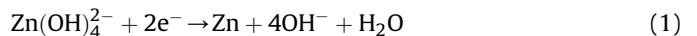


Fig. 2. (a) The XRD pattern of as-prepared ZnAl-hydrotalcites, (b) the typical SEM images of ZnAl-hydrotalcites.

zinc electrode. The electrolyte was 6 M KOH solution, different from that used in cycling test. The change of the electrolyte is based on the consideration of the following reasons. In CV experiment, it explores the micro reaction of the electrode surface, instead of internal reaction of the electrode in depth. And it needs short time to complete the test. Thus, the influence of the solubility of ZnO in 6 M KOH solution was not obvious. However, in cycling test, the internal reaction of the electrode would carry out deeply that may take long time. Therefore, the influence of ZnO solubility in the alkaline electrolyte cannot be neglected. In order to prevent the solubility of ZnO in 6 M KOH solution, the mixed alkali is introduced and regarded as the electrolyte used in the cell. As shown in Fig. 3, the potential sweep starts from -1.05 V, going in the cathodic direction. The ZnO electrode is coded A electrode, and ZnAl-hydrotalcites electrodes, whose Zn/Al (molar ratio) is 3/1, 4/1 and 5/1 respectively, are coded B, C and D electrodes. In Fig. 3, on the first cathodic scan, a single reduction peak of zinc electrodes containing ZnAl-hydrotalcites appears at -1.43 V, and the position and shape of cathodic peak are very close to the cathodic peak of the electrochemical reduction of ZnO [12–15] which appears at -1.41 V. It is well known that a more negative potential means a lower electrochemical kinetics of reduction process. The only difference is that the potential is positively shifted by about 20 mV,

indicating a lower polarization. When the potential scan is reversed into the more positive region, two anodic peaks of zinc electrodes containing ZnAl-hydrotalcites appear at about -1.35 and -1.32 V, respectively, which was shifted in the more negative direction in comparison with that (-1.29 V) of ZnO. The electrode reaction and the well-known Nernst equation are as follows:



$$\Phi = \varphi^\phi + (0.0592/2)\lg([\text{Zn}(\text{OH})_4^{2-}]/[\text{OH}^-]^4);$$

$$\varphi^\phi = -1.249,$$

The standard electrode potential of zinc electrode with ZnAl-hydrotalcites is in accord with CV result. Obviously, the anodic peak potential of the electrode C containing ZnAl-hydrotalcites with Zn/Al = 4/1 (molar ratio) increases compared with the electrode containing ZnO. As we know, the anodic process corresponds to the discharge process of the zinc electrode. The higher of the current of anode peak indicate the high oxidation activity for ZnAl-hydrotalcites (molar ratio = 4/1) electrode. This phenomenon reveals that the reversibility of the reaction:



become much better in this system, which is probably attributed to the lamellar structure of ZnAl-hydrotalcites and the presence of aluminum ions. The aluminum ions may aid zinc to form nuclei during deposition, so as to deplete overgrowth of zinc grain, such as zinc moss and dendrites [11,16]. Consequently, dendritic growth of zinc electrode is restricted and thus the electrochemical performance is improved. Simultaneously, the potential positions and relative intensities of these two anodic peaks are in accordance with the CV features for anodic oxidation process of metal Zn in KOH solution [5]. A higher anodic current of zinc electrode containing ZnAl-hydrotalcites implies that the anodic process is easier and higher electrochemical activity. Furthermore, the two anodic peaks may be attributed to the anodic dissolution of zinc to form $\text{Zn}(\text{OH})_4^{2-}$ and $\text{Zn}(\text{OH})_3^-$, consistent with the previous work [17–19]. The two anodic peaks correspond to two processes of anodic dissolution. There is no doubt that the reaction at the equilibrium potential results in the zincate ion, $\text{Zn}(\text{OH})_4^{2-}$, by a probable three-step process represented by the overall reaction [18,19]. Equation (3) is the most the major oxidation reaction and must be the one occurring in the first peak a.

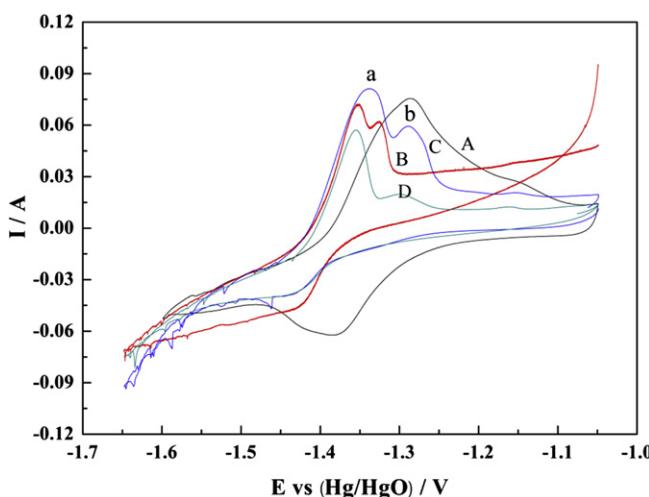
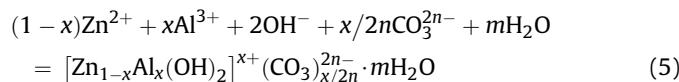


Fig. 3. Cyclic voltammogram for zinc electrodes with ZnO and different Zn/Al molar ratios of ZnAl-hydrotalcites. A: ZnO. B: Zn/Al = 3:1. C: Zn/Al = 4:1. D: Zn/Al = 5:1.



When the reaction (3) has been proceeding for some time at a lower over-potential and consequently when there has been an inadequate contact between the active zinc and OH^- ion from the reaction layer. Equation (4) will perform and the second peak b occurs. The two anodic peaks caused by the inadequate contact were ever reported [18,19]. A probable reaction corresponding to this peak b is represented by Equation (4).

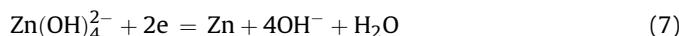
As mentioned above, the inadequate contact could be induced by the aluminum ions. To sum up the above arguments, the reaction can be described as Equation (5).



In the discharging process, the deposited zinc would lose electrons to form zincate anions in the alkaline environment which are favorable for reformation of ZnAl-hydrotalcites and thus result in high reversibility.

3.4. Galvanostatic charge and discharge properties

The typical galvanostatic charge/discharge curves of Zn/Ni cells with the ZnO and ZnAl-hydrotalcites at the 20th cycle are displayed in Fig. 4. The overall electrode reaction can be described as Equations (6) and (7).



From Fig. 4a, it can be seen that Zn/Ni cells with ZnAl-hydrotalcites show a higher charge plateau than ZnO. The main reason is that ZnAl-hydrotalcites have poor conductivity, in other words, the cell with ZnAl-hydrotalcites electrode has a large internal resistance. Meanwhile, two higher charge plateaus can be observed for Zn/Ni cells with ZnAl-hydrotalcites, whereas, there is only one lower charge plateau at 1.85 V for ZnO electrode (code A). The first charge plateau is *ca.* 1.85 V for ZnAl-hydrotalcites electrodes, but the voltage rises rapidly in the later charging process and the charge plateau is nearby 1.95 V for ZnAl–CO₃–LDHs with Zn/Al = 3/1 (molar ratio) (code B) and 4/1 (code C) and at 1.97 V for ZnAl–CO₃–LDH with Zn/Al = 5/1 (molar ratio) (code D). In contrast, the voltage rising velocity is: electrode D > electrode B > electrode C. This may be explained as the insufficient electronic contact and a higher internal resistance, resulting from the two dimensional layered structure, which is also revealed in CV result.

Meanwhile, as shown in Fig. 4b, discharge plateau voltage is *ca.* 1.7 V. Although the discharge time of electrode C is a little shorter, the discharge plateau voltage of electrode C is higher than the electrode A, as revealed conformably in Fig. 3. From Fig. 4b, the discharge plateau voltage for electrodes B and D containing ZnAl-hydrotalcites decreased with Zn/Al = 3/1 and 5/1 (molar ratio), which indicates that aluminum hydroxide on the layered structure has an impeditive effect on the electrochemical oxidized reactions of Zn. The impeditive effect should be associated with the decrease of direct contact between zinc active materials with the electrolyte. However, it should be noted that this phenomenon has no undesirable influence on the discharge capacity of Zn/Ni cells. It suggests that aluminum hydroxide on the layered structure only influences electrochemical reaction rate to a certain extent and leads to

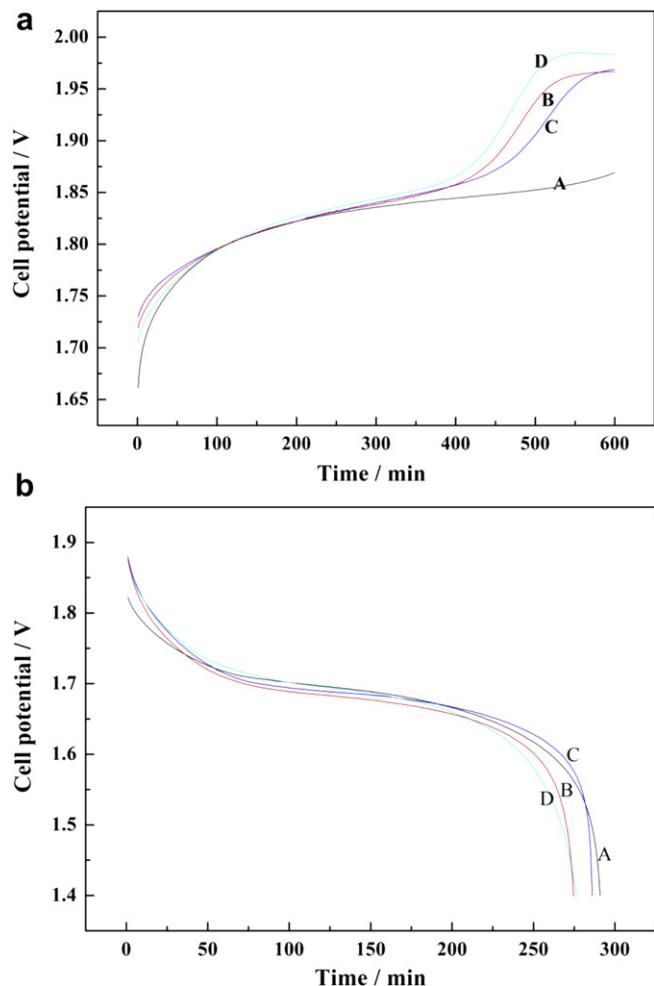


Fig. 4. Typical galvanostatic charge curves (a) and discharge curves (b) of Nickel–Zinc secondary cells with ZnO and different Zn/Al molar ratio of ZnAl-hydrotalcites at the 20th cycle. A: ZnO. B: Zn/Al = 3:1. C: Zn/Al = 4:1. D: Zn/Al = 5:1.

a lower electrochemical kinetics [3]. The decrease in electrochemical kinetics is a favorable phenomenon to improve electrochemical stability of ZnAl-hydrotalcites, which is confirmed by the following cyclic tests.

The variation of discharge capacity with number of cycles for electrode containing ZnO and ZnAl-hydrotalcites are depicted in Fig. 5a ZnAl-hydrotalcites deliver an initial discharge capacity of 400 mAh g⁻¹ and has capacity retention ratio of 92.7% over 50 cycles. On the other hand, the initial discharge capacity of ZnO (code A) is 467 mAh g⁻¹ and the capacity retention ratio is 51.1%. The poor cycling stability is attributed to the solubility of ZnO. Although Zn–Al-hydrotalcite electrode has lower specific capacity than ZnO electrode, they have excellent electrochemical cycling stability and higher utilization ratio in alkaline solution. For comparison, the discharge capacity of ZnAl-hydrotalcites with Zn/Al = 3/1 (molar ratio) (code B) is relatively lower due to its lower theoretical capacity (413.3 mAh g⁻¹). For ZnAl-hydrotalcites with Zn/Al (molar ratio) = 4/1 (code C) and 5/1 (code D), the discharge capacity was declined more uniform. In the last ten cycles, the discharge capacity of electrode D is decayed slightly faster. Several factors could be responsible for this phenomenon. As to ZnAl-hydrotalcites, their alkaline characteristics were the most fundamental guarantee for application in the Nickel–Zinc secondary cells, so that the novel anodic material is in the nature of the stability in alkaline electrolyte. In

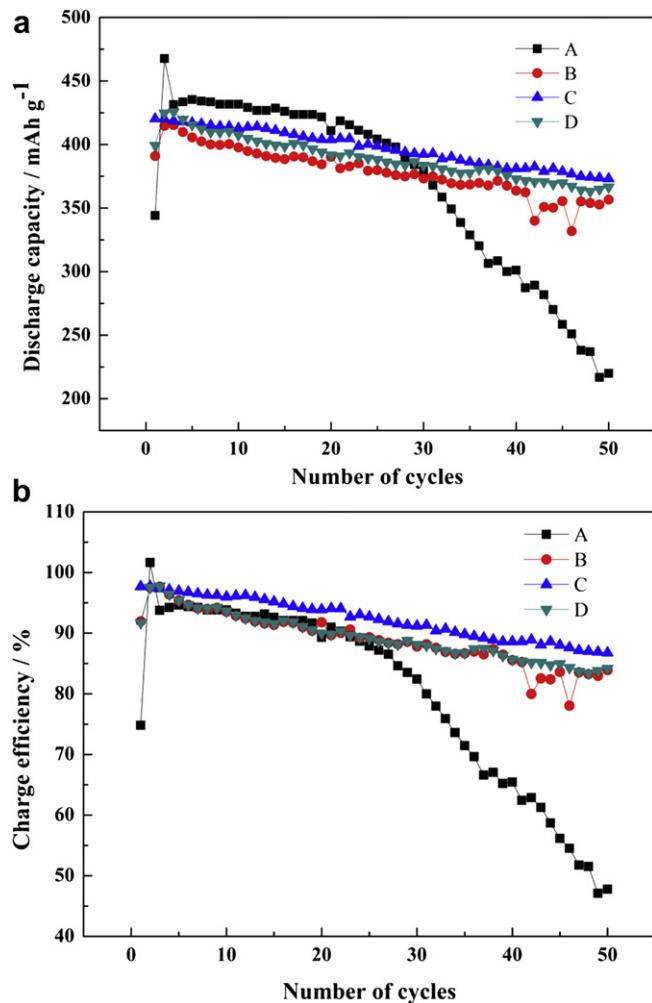


Fig. 5. (a) The variation of discharge capacity with number of cycles for electrodes with ZnO and different Zn/Al molar ratios of ZnAl-hydrotalcites. A: ZnO. B: Zn/Al = 3:1. C: Zn/Al = 4:1. D: Zn/Al = 5:1. (b) The variation of charge efficiency with number of cycles for electrodes with ZnO and different Zn/Al molar ratios of ZnAl-hydrotalcites. A: ZnO. B: Zn/Al = 3:1. C: Zn/Al = 4:1. D: Zn/Al = 5:1.

the two dimensional layered structure, the zinc hydroxide was arranged orderly on a layer and aluminum hydroxide was on the other parallel layer. These properties may relieve shape change of zinc electrode and dendrite growth during the charge/discharge cycling. The existed aluminum ions may not only reduce the resistivity of zinc active materials but also enhance the electrical conductivity of zinc electrode [9–11]. Simultaneously, aluminum ions are conducive to zinc active material to form crystal nucleus for the electrodeposition of zinc, so that the growth of grain is effectively controlled. Consequently, the higher discharge capacity could be enhanced.

The variation of charge efficiency with number of cycles for electrode containing ZnO and ZnAl-hydrotalcites is shown in Fig. 5b. The charge efficiency gradually decrease with increasing number of cycles in all case after activating. The charge efficiency of ZnO electrode is 46.79% after 50 cycles owing to the solubility of ZnO. However, the charge efficiency of ZnAl-hydrotalcites electrode is above 80% over 50 cycles. In particular, the charge efficiency of ZnAl-hydrotalcites with Zn/Al = 4/1 (molar ratio) (code c) is 86.75% over 50 cycles, which is much better than ZnO. The most probable reason is that the Zn–Al-hydrotalcite is more stable than ZnO in the alkaline solution. From the point of view of cyclic stability and

charge efficiency, ZnAl-hydrotalcites is an excellent electrode material for Ni–Zn secondary cell.

Fig. 6 shows the XRD patterns of ZnAl-hydrotalcites electrode after 50 charge/discharge cycles. The peak of ZnAl-hydrotalcites has the highest intensity and the shape is not changed, indicating that the ZnAl-hydrotalcites still have good structural and crystalline after 50 charge/discharge cycles. The active material of ZnAl-hydrotalcites electrode remains existence of layered structure during the charge/discharge cycling. Results above show that ZnAl-hydrotalcites are more stable than ZnO in charge/discharge process. The XRD pattern in Fig. 6 also contains diffraction peaks corresponding with ZnO and Al₂O₃, which is ascribed to the crystalline ZnO and Al₂O₃ generated from ZnAl-hydrotalcites on the discharge process. From the absence of Al₂O₃ in electrode, it can be deduced that Zn in Zn–Al-hydrotalcite also takes part in the electrochemistry reaction during the discharge process. In addition to ZnO and Al₂O₃, it also contains peaks corresponding to Zn, binder and Cu. Apparently, Cu is derived from the copper mesh substrate.

3.5. The average internal resistance of the Ni–Zn cell with ZnO and ZnAl–CO₃–LDHs

Fig. 7 displays the average internal resistance curves of the Ni–Zn cell with ZnO and ZnAl-hydrotalcites. As can be seen, the cell with ZnO and ZnAl-hydrotalcites exhibits the average internal resistance between 30 mΩ and 40 mΩ. In contrast, the internal resistance variation of electrode A is relatively lower but unstable, which might be due to zinc dendrite. It could easily penetrate the separators and result in the interior short circuit. As to electrodes B, C and D, electrode B has a higher internal resistance. The electrodes C and D have relatively lower internal resistance but great variety for electrode D. This phenomenon could be ascribed to the following reasons. In the ZnAl-hydrotalcites with Zn/Al (molar ratio) = 3/1, the high amount of aluminum content could cause active area decrease so that insufficient electrical contact could lead to a higher internal resistance. However, due to the low amount of aluminum content in the ZnAl-hydrotalcites with Zn/Al (molar ratio) = 5/1, it was difficult to maintain the layered structural integrity during charge and discharge process. Therefore, the internal resistance was unstable. In the electrode C containing ZnAl-hydrotalcites with Zn/Al (molar ratio) = 4/1, the appropriate Zn/Al (molar ratio) was the guarantee for ideal active area and

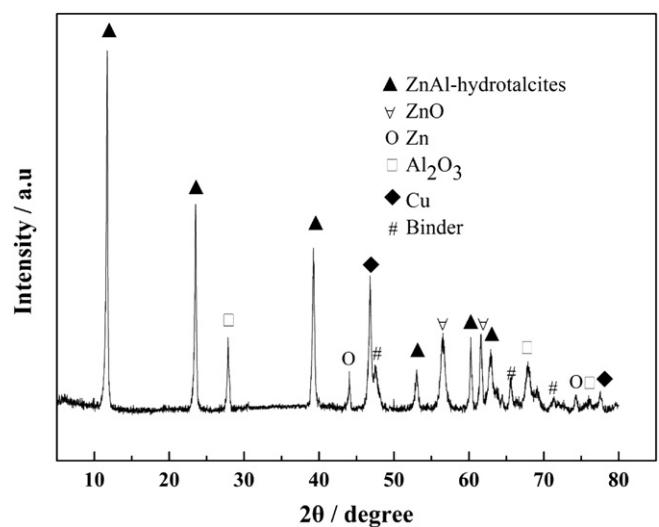


Fig. 6. XRD pattern of the ZnAl-hydrotalcites (Zn/Al molar ratio is 4:1) electrode after complete discharge over 50 cycles.

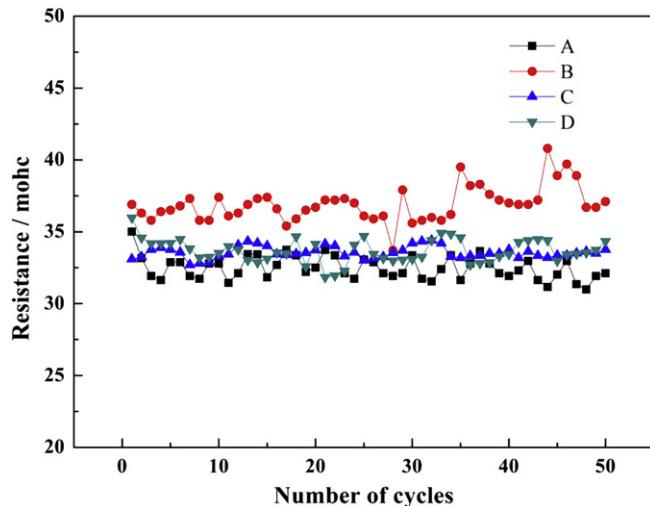


Fig. 7. The average internal resistance curve of the Nickel–Zinc secondary cell with ZnO and different Zn/Al molar ratios of ZnAl-hydrotalcites. A: ZnO. B: Zn/Al = 3:1. C: Zn/Al = 4:1. D: Zn/Al = 5:1.

stable layered structure during charge and discharge process. This indicates that the electrode C is more stable in the solution and has the best reversibility during the cycling as revealed in Fig. 5.

4. Conclusions

ZnAl-hydrotalcites with different Zn/Al molar ratio have been fabricated by co-precipitation method. The structure and electrochemical performance of Ni–Zn secondary cell with ZnAl-hydrotalcites as the negative electrode is investigated. ZnAl-hydrotalcites is highly crystallized to be a rounded hexagonal crystal structure. ZnAl-hydrotalcites with different Zn/Al molar ratio, especially the sample of Zn/Al = 4/1 (molar ratio), employed as negative electrode of Ni–Zn battery exhibits good reversibility,

superior electrochemical cycling stability and more excellent utilization ration in the alkaline solution compared with the ZnO electrode. Therefore, ZnAl-hydrotalcites were good and novel active materials for Ni–Zn secondary cells.

Acknowledgments

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